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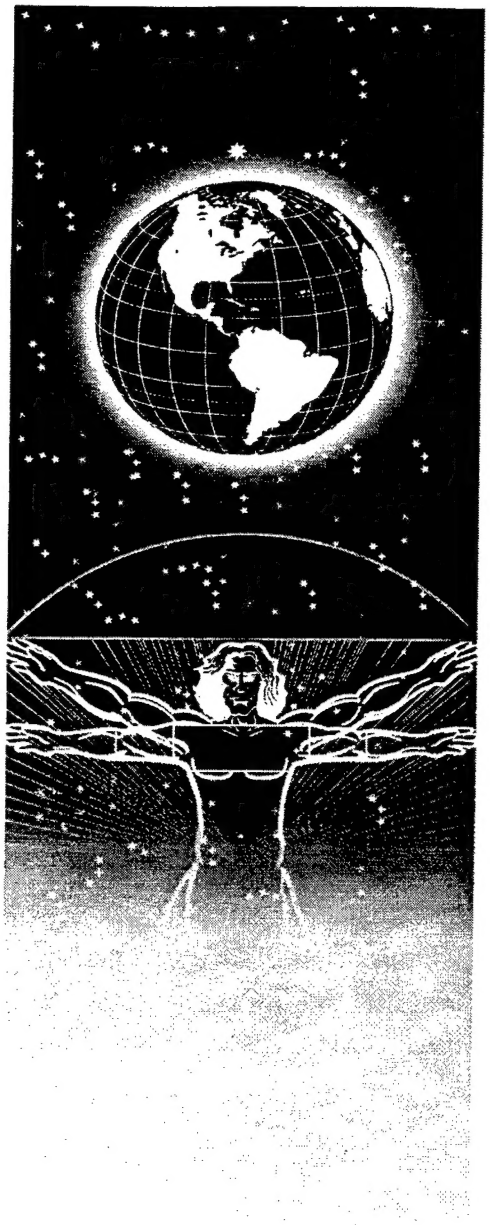

UNITED STATES AIR FORCE ARMSTRONG LABORATORY

Effect of Dissolved Matter on Fe (II) Transport in Groundwater

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February, 1997

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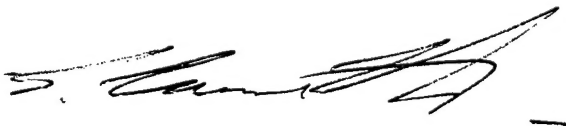

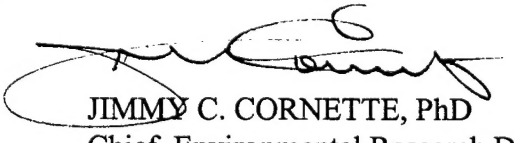

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14. Abstract

As the focus of ground water remediation efforts shifts increasingly towards natural attenuation as an alternative method for documenting and quantifying such intrinsic remediation. One indicator of natural attenuation under iron-reducing conditions is concentration of dissolved Fe(II). However, if Fe(II) is to be used to quantify the degradation of groundwater contaminants the process controlling Fe(II) transport in the subsurface must be better understood.

Dissolved metals, such as Fe (II) can interact with dissolved organic matter (DOM) to produce both mobile and immobile complexes. These complexes may display sorptive characteristics different than those of the dissolved metal alone, thus potentially facilitating or retarding transport of the metal. Microcosm sorption studies were conducted to determine the effects of DOM on Fe(II) sorption to aquifer solids from 3 U.S. Air Force Bases as a function of ionic strength (I). DOM at a concentration of 32 mg TOC/L resulted in a marked increase in the sorption of Fe(II) to each of the aquifer solids at I=0.01 M, as judged by Freundlich non-linear isotherm fits of the data. Sorption of Fe(II) in the presence of DOM at I=0.1 also increased over that of DOM-free systems but was less than that in the I=0.01 systems, indicating an inverse relationship between Fe(II) sorption and ionic strength.

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PREFACE

This report was prepared as part of the Air Force Office of Scientific Research Summer Faculty Research Program sponsored by Armstrong Laboratory's Environics Directorate, Tyndall Air Force Base, Florida 32403.

The report covers research performed by Eric J. Henry, Graduate Student at Washington State University, between June and August 1988. The report is being reprinted and sent to Defense Technical Information Center because of its interest to the DOD and worldwide scientific and engineering communities. The AL/EQ mentor was Dr. E. Laurance Libelo. The AL/EQ Summer Faculty Coordinator was Ms. Mary Reynolds.

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Dissolved metals, such as Fe(II) can interact with dissolved organic matter (DOM) to produce both mobile and immobile complexes. These complexes may display sorptive characteristics different than those of the dissolved metal alone, thus potentially facilitating or retarding transport of the metal. Microcosm sorption studies were conducted to determine the effects of DOM on Fe(II) sorption to aquifer solids from 3 U.S. Air Force Bases as a function of ionic strength (I). DOM at a concentration of 32 mg TOC/L resulted in a marked increase in the sorption of Fe(II) to each of the aquifer solids at I = 0.01 M, as judged by Freundlich non-linear isotherm fits of the data. Sorption of Fe(II) in the presence of DOM at I = 0.1 also increased over that of DOM-free systems but was less than that in the I = 0.01 systems, indicating a inverse relationship between Fe(II) sorption and ionic strength.

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EFFECT OF DISSOLVED ORGANIC MATTER ON Fe(II) TRANSPORT IN GROUNDWATER

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Introduction

As the focus of groundwater remediation efforts shifts increasingly towards natural attenuation as an alternative method for subsurface restoration, a great deal of research must now focus on methods for documenting and quantifying such intrinsic remediation. One indicator of natural attenuation under iron-reducing conditions is concentration of dissolved Fe(II). During the microbial degradation of organic contaminants in anaerobic systems with Fe(III) the electron acceptor, Fe(III) is reduced to Fe(II), and Fe(II) concentrations increase (Wiedemeier *et al.*, 1995). Fe(II) can be used to quantify the degradation of groundwater contaminants if the processes controlling Fe(II) transport in the subsurface are understood.

Sorption has been identified as having a potentially significant effect on the transport of metals in the subsurface (Coughlin and Stone, 1995). Additionally, dissolved metals, such as Fe(II) can interact with dissolved organic matter (DOM) to produce both mobile and immobile complexes. These complexes may enhance or decrease sorption distribution between dissolved and solid phases, thus potentially facilitating or retarding transport of the metal. The ability of DOM, such as natural humic substances, to perform in this regard is dependent upon contaminant-humic, contaminant-sediment, and humic-sediment affinities as well as the kinetics of each of these interactions (Johnson and Amy, 1995). The strong affinity for metals to form complexes with humic substances has been well documented (Sposito, 1986; Perdue, 1989; Oden *et al.*, 1993; Benedetti *et al.*, 1995), and therefore a humic acid was chosen as a representative DOM for this investigation. Piana (1995) has described the sorption of Aldrich Humic Acid (AHA) onto aquifer solids from three U.S. Air Force Bases: Columbus AFB, Mississippi, Barkesdale AFB, Louisiana and Blytheville AFB, Arkansas, and Libelo (in prep.) has described the sorption of Fe(II) onto the same three aquifer solids. In order to supplement the data collected by Libelo and Piana, and maximize the relevancy of this research project, it was decided to investigate the effect of AHA on Fe(II) sorption onto the same aquifer solids.

Materials and Methods

General Description:

Batch sorption studies were conducted on three aquifer solids at two ionic strengths to describe the effect of natural organic matter on Fe(II) sorption. Dialysis tubing was used to achieve phase separation between the free ferrous ion and the ferrous-organic complex in order to describe the partitioning of Fe(II) to the humic acid. All experiments were carried out in 20 mL glass serum vials under anaerobic conditions to ensure that decreases in the aqueous Fe(II) concentration due to oxidation to Fe(III) were negligible. Anaerobic conditions were established and maintained either through bench-top nitrogen purging or operation within an anaerobic glove box. All solutions and dilution waters were nitrogen purged for 1 hour before use.

Aquifer Solids:

The substrates investigated in this study were obtained from Dr. T. Stauffer, Armstrong Laboratory, Tyndall AFB, FL, and consisted of unconsolidated sediments from aquifers at 3 Air Force Bases: Columbus AFB, Mississippi, Barkesdale AFB, Louisiana and Blytheville AFB, Arkansas. Specifically, the fraction of each sediment less than 2 millimeters was used in these experiments. Stauffer (1987) and Libelo (1995) have characterized each of the sediments and a summary is presented in Table 1.

Ionic Strength:

McCarthy and Zachara (1989) note that solution chemistry, including ionic strength and pH, can have an impact on contaminant sorption, and that such issues remain as areas which merit additional investigation. A number of researchers, including Westall *et al.* (1995), and Zachara *et al.* (1994) have shown metal sorption and complexation with humic acid to be a function of the geochemistry of the system. To determine the impact of ionic strength on Fe(II) sorption, all experiments described in this report were performed in ionic strength buffers of 0.01 and 0.1 M sodium perchlorate ($NaClO_4$) dissolved in Milli-Q ($\approx$18MΩ) water. In the interest of time and in order to keep the chemistry of the experimental systems as

simple as possible to avoid possible buffer ion effects, no controls on pH were instituted. The pH of the samples following equilibration was measured and ranged from 4.5-5.5.

Humic Acid Solutions and Analysis:

Aldrich Humic Acid (Aldrich, Milwaukee, WI) was used as a representative dissolved organic matter. 1000 mg/L humic acid solutions were prepared in ionic strength buffer solutions of 0.1 M and 0.01 M $NaClO_4$. Preliminary experiments showed the dissolved AHA to be approximately 32 % total organic carbon (TOC) by weight. All TOC measurements were made using a Shimadzu TOC-5000 combustion/non-disperse infrared gas analysis system (Shimadzu Corp., Kyoto, Japan). Kim *et al.*, (1990) provide further characterization of Aldrich HA which is summarized in Table 2.

Most groundwaters have dissolved organic carbon concentrations below 2 mg C/L, with a median value of about 0.7 mg C/L (Leenheer *et al.*, 1974, referenced by Drever, 1988). Aiken *et al.* (1985, referenced by Piana, 1995) report TOC values of natural waters between 1 and 30 mg C/L. A total organic carbon value at the high end of typical values, 32 mg C/L, was used for all experiments. It was expected that any variation in the sorption characteristics of Fe(II) due to the presence of DOM would increase with increasing TOC concentration and the use of a high concentration of TOC should therefore make those effects more pronounced and easily identified.

Fe(II) Solutions and Analysis:

Ferrous iron stock solutions were prepared by dissolving ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2$, in 0.1 and 0.01 M ionic strength buffers under nitrogen gas purge. Analysis of aqueous Fe(II) was conducted using a variation of the Ferrozine method described by Stookey (1970) and Gibbs (1976). Briefly, Ferrozine reagent forms a complex with Fe(II) which allows spectrophotometric analysis with the maximum absorbance occurring at a wavelength of 562 nanometers.

Ferrozine reagent was prepared by dissolving approximately 12 grams of HEPES buffer and 1 gram of Ferrozine (Aldrich) and diluting to 1 liter with Milli-Q water. Serial dilutions of the Fe(II) stock solutions were made, again using nitrogen purged ionic strength solutions, and a calibration curve developed. All

calibration standards, as well experimental samples, were prepared prior to analysis by the addition of 100 microliters of sample to 2 mL of Ferrozine reagent in a glass sample vial. Analyses were performed using a Cary 3E UV-Visible Spectrophotometer (Varian Instruments). The calibration curve was found to be linear throughout the range of interest for these experiments (0-100 mg Fe(II)/L).

Dialysis Tubing:

The molecular weights of dissolved organic matter range from 500 to 30,000 (Amy *et al.*, 1992). Particles within this size range are not settleable using centrifugation and therefore it was necessary to utilize another technique to obtain phase separation between ferrous ion in the free ion form, denoted Fe^{2+}, and that which is complexed with HA, denoted Fe^{2+}-HA. Dialysis tubing was chosen for phase separation because it is available in molecular weight cutoffs (MWCO) as low as 1000 and other researchers have shown it to be both effective for HA separation (Carter and Suffet, 1982; Zachara *et al.*, 1994) and durable within a system containing sediment (Allen-King *et al.*, 1995). Additionally, dialysis tubing has the advantage of achieving phase separation and equilibration simultaneously.

Spectra/Por 7, Regenerated Cellulose Membrane Dialysis Tubing, MWCO = 1000, flat width = 18 mm, was chosen for use because it is free of heavy metals and may be easily sealed by tying. The tubing is packaged in a dilute solution of sodium azide and required rinsing before use. The rinsing procedure consisted of placing the tubing in a 600 mL beaker filled with Milli-Q water, shaking the beaker for 1 minute, and then pouring the water into a waste container. This procedure was repeated 5 times. When not in use, rinsed tubing was stored in Milli-Q water.

Following rinsing, the dialysis tubing was cut into 16 centimeter lengths and one end tied. The tubing was then opened and 3 mL of ionic strength solution, appropriate to the given experiment, was pipetted into the tubing and the open end tied, forming a dialysis 'bag'. Excess tubing was trimmed away before placing the dialysis bag into the sample vials. An illustrative description of the experimental setup is shown in figure 1.

Rate Experiments:

Equilibrium is reached within 24 hours with regard to both HA sorption and Fe(II) sorption to each of the 3 substrates (Piana, 1995; Libelo, in prep.). Therefore, so that the experimental run time could be minimized, it was desired to show that the diffusion of Fe(II) through the bag reached equilibrium within 24 hours. The time required for diffusion equilibrium was determined by placing a dialysis bag filled with 5 mL of 0.1 M ionic strength solution into a sample vial containing 14 mL of 60 mg/L Fe(II) solution. Enough vials were prepared in this manner to allow sampling at 4 different times, in triplicate. At time increments of 1, 2, 4, and 7 days, samples were withdrawn from the inside and outside of the bag. Change in Fe(II) concentration within the bag was not detectable at times greater than 1 day, thus an equilibration period of 1 day was deemed to be satisfactory.

Analogous experiments were conducted to ensure that diffusion of AHA through the bag within the 1 day equilibration period was negligible. The TOC concentration within the bag after 1 day was approximately 5.5 % of the total TOC in the system. Comparison to controls indicated an increase with time in the total TOC present in the systems which contained dialysis bags even though the outer TOC concentration did not increase noticeably. This suggests that the TOC within the bag was derived from the dialysis tubing and AHA diffusion was deemed negligible.

Equilibrium Adsorption Isotherms:

Fe(II) sorption isotherms were developed at a constant TOC of 32 mg C/L, at ionic strengths of 0.01 and 0.1, in triplicate. Ferrous iron solutions were made at five different concentrations (approximately 75, 57, 38, 19, and 8 mg Fe(II)/L). Two grams of sediment, 1.4 mL of 1000 mg/L humic acid (320 mg C/L), and 12.6 mL of the appropriate ferrous iron solution were added to a 20 mL serum vial. A dialysis bag was then filled with 3 mL of ionic strength solution, placed in the vial, and the vial sealed. Controls were also prepared at the same dilutions, without sediment or humic acids.

Following 1 day equilibration on a rotary shaker, samples were removed and centrifuged (Damon/IEC EPR-6000) at 2000 rpm for 5 minutes. The solutions from inside and outside the dialysis bag

were then extracted using a volumetric syringe and 100 uL of each sample filtered (0.45 um) and added to 2 mL of Ferrozine for Fe(II) analysis. Following spectrophotometric analysis of all samples the total mass of Fe(II) added to each vial was determined using controls. The concentration of Fe(II) sorbed was then calculated using a mass balance and isotherms developed.

Sorption to solid substrates is often described as a linear partitioning of the contaminant between aqueous and solid phases:

$$C_s = K_d C_w \qquad (1)$$

where, Cs and Cw are the concentrations of the solute sorbed to the solid and dissolved in water, respectively, and Kd is the partitioning coefficient. Such a distribution assumes that sorption is independent of contaminant concentration and is defined as a linear isotherm. Frequently, however, a distribution of contaminant between the aqueous and solid phase which is non-linear with respect to the dissolved species is observed (Grathwohl, 1990). These non-linear partitioning distributions may be described using the Freundlich isotherm, equation 2:

$$Cs = K_f C_w^{1/n} \qquad (2)$$

where Cs and C_w are as defined as above, K_f is the Freundlich partitioning coefficient, and 1/n is a constant describing the dependence on solute concentration. The data from these experiments were fit with each type of isotherm and the results are presented in the following section.

Results And Discussion

At a TOC concentration of 32 mg/L, there was no statistical difference between the Fe(II) concentrations inside and outside of the dialysis bag. It was not possible, therefore, to describe the partitioning between of Fe(II) between the free ion phase, Fe^{2+}, and the humic complexed phase, Fe^{2+}-HA. The overall effect of AHA on Fe(II) sorption can be evaluated by the comparison of isotherms from systems containing AHA to isotherms from HA-free systems. The data from the HA-free systems have been kindly provided by Libelo (personal communication). In all systems (fixed HA concentration, fixed ionic strength) the order of decreasing affinity for Fe(II) sorption as a result of substrate type proceeds as Blytheville >

Columbus > Barkesdale. As an example, the isotherms for each substrate in an I = 0.01 system containing HA are given in figure 2.

The sorption isotherms depicted in figures 3 through 8 graphically illustrate the influence of HA on Fe(II) sorption at I = 0.01 and I = 0.1. The data were also modeled using linear and Freundlich isotherm expressions and the results are given in table 3. As judged by the r^2 values, the Freundlich isotherm typically yields the best fit and further discussion of the characteristic curves will be based on the Freundlich parameters.

Because both the K_f and 1/n values differ for each set of experiments it is difficult to compare the systems simply based on these values. As a semi-quantitative means of comparison, the sorbed equilibrium concentration was calculated according to the Freundlich equation corresponding to a dissolved Fe(II) concentration of 15 mg/L and these values are given in table 3. This concentration was chosen as an approximation of Fe(II) values occurring within an iron reducing environment of a polluted aquifer as reported by Albrechtsen and Christensen (1994).

From the graphs (3-8) it may be observed that the effect of AHA at low concentrations of Fe(II) is minimal, as should be expected according to both isotherm models. Of interest, however, is the trend which may be observed at increasing Fe(II) concentrations. Figures 3, 5, 7, and 8 reveal an marked increase in sorption of Fe(II) in the presence of AHA over that of HA-free systems. This conclusion is also supported by the calculated estimates of C_s in table 3. Some difficulty is associated with the use of figures 6 and 8 for supposition because the two isotherms being compared in each case encompass greatly varying Fe(II) concentrations.

Figures 9 through 11 contain all 4 isotherms (I = 0.1 and 0.01, 32 mg C/L and No AHA) for each substrate, and suggest that the sorption of Fe(II) in the presence of AHA decreases with increasing ionic strength. Other researchers have also shown this to be the case in metal-organic systems (Zachara *et al.*, 1994; Westall *et al.*, 1995) and associated this decrease in sorption with an decrease in the affinity of the organic for complexation with the dissolved metal at higher ionic strengths.

Conclusions and Recommendations for Future Work

The presence of dissolved organic matter has been shown to increase the sorption of dissolved Fe(II) to aquifer solids. This effect is enhanced as the ionic strength of the system decreases. The implication these results have for the use of dissolved Fe(II) as an indicator of natural attenuation is that measured Fe(II) concentrations in groundwater may underpredict the true production of Fe(II) during microbial degradation of organic contaminants under iron reducing conditions. Though this underprediction would yield a conservative estimate of the time necessary to achieve adequate remediation, such estimates are inefficient and may result in wasted time, money, and resources.

In order to obtain the best possible estimates of contaminant degradation rates additional research must be conducted to determine the effects of system geochemistry, including pH, redox, and the presence of competing sorbates on Fe(II) sorption in the presence of dissolved organic matter. Once such data is collected it should be possible to combine it with the data base already established by Piana (1995) and Libelo (in prep) to model Fe(II) sorption dynamics in the subsurface.

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Table 1. Characteristics of Aquifer Sediments

Aquifer	Total Organic Carbon %	Surface Area m^2/g	Dithionate Extractable Iron g/kg	% Sand	% Silt	% Clay
Barkesdale	0.0338	0.88	0.112	96.1	1.94	1.97
Blytheville	0.0676	9.32	1.640	95.6	3.06	1.34
Columbus	0.0596	5.78	0.914	70.8	17.50	11.68

Table 2. Elemental Composition and Physical Properties of Aldrich Humic Acid

C	H	N	S	O	Other	H/C ratio	O/C ratio	Aromatic C (110-165)	Aliphatic C (0-90)	Carboxyl C (165-190) PPM
41.72	4.37	0.25	1.90	36.93	14.83	1.03	0.51	40	41	14

Table 3. Linear and Freundlich Isotherm Parameters

Sediment	Condition	log K_f[a]	1/n[a]	r^2	C_s[b]	Kd[c]	r^2	n[d]
Barkesdale	No HA, I=.01	1.084 (1.052-1.116)	0.512 (.476-.549)	0.985	48.6	2.52	0.93	16
	HA, I=.01	1.182 (1.132-1.233)	0.646 (.603-.690)	0.987	87.4	3.58	0.94	15
	No HA, I=.1	1.350 (1.212-1.488)	0.336 (.279-.402)	0.903	55.6	0.26	0.76	15
	HA, I=.1	1.182 (1.011-1.354)	0.431 (.289-.573)	0.860	48.9	1.39	0.75	10
Blytheville	No HA, I=.01	1.693 (1.591-1796)	0.207 (.033-.381)	0.530	86.4	5.53	0.76	9
	HA, I=.01	1.734 (1.680-1.788)	0.539 (.476-.602)	0.963	233.3	10.61	0.93	15
	No HA, I=.1	1.722 (1.622-1.822)	0.307 (.260-.354)	0.992	121.1	0.30	0.74	18
	HA, I=.1	1.550 (1.411-1.689)	0.536 (.395-.676)	0.906	151.5	8.05	0.85	10
Columbus	No HA, I=.01	1.124 (1.101-1.180)	0.590 (.564-.617)	0.993	65.8	4.32	0.95	19
	HA, I=.01	1.516 (1.485-1.548)	0.502 (.471-.533)	0.990	127.8	4.52	0.91	15
	No HA, I=.1	1.244 (.942-1.545)	0.336 (.204-.468)	0.646	43.6	0.65	0.25	18
	HA, I=.1	0.957 (.915-.999)	0.646 (.612-.681)	0.992	52.1	2.08	0.97	15

a.) 95% confidence interval in brackets; b.) sorbed concentration, C_s, at C_w = 15 mg Fe(II)/L calculated using Freundlich isotherm coefficients; c.) linear isotherm not forced through zero; d.) n =number of samples

Figure 1. Schematic Drawing of Equilibrium Sorption Experiment Setup

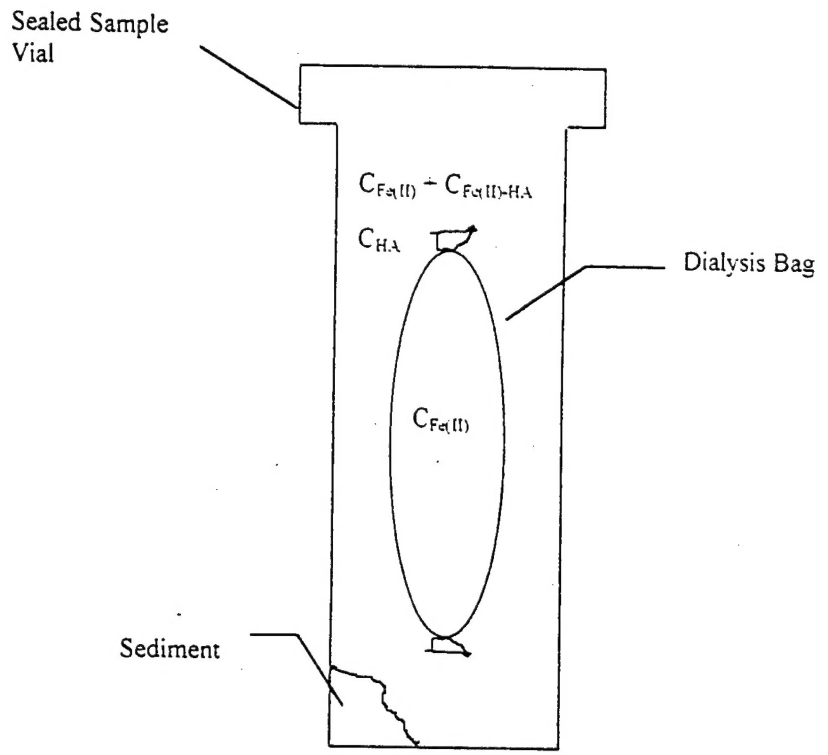

Figure 2. Example Fe(II) Sorption Isotherm
TOC = 32 mg/L, I = 0.01

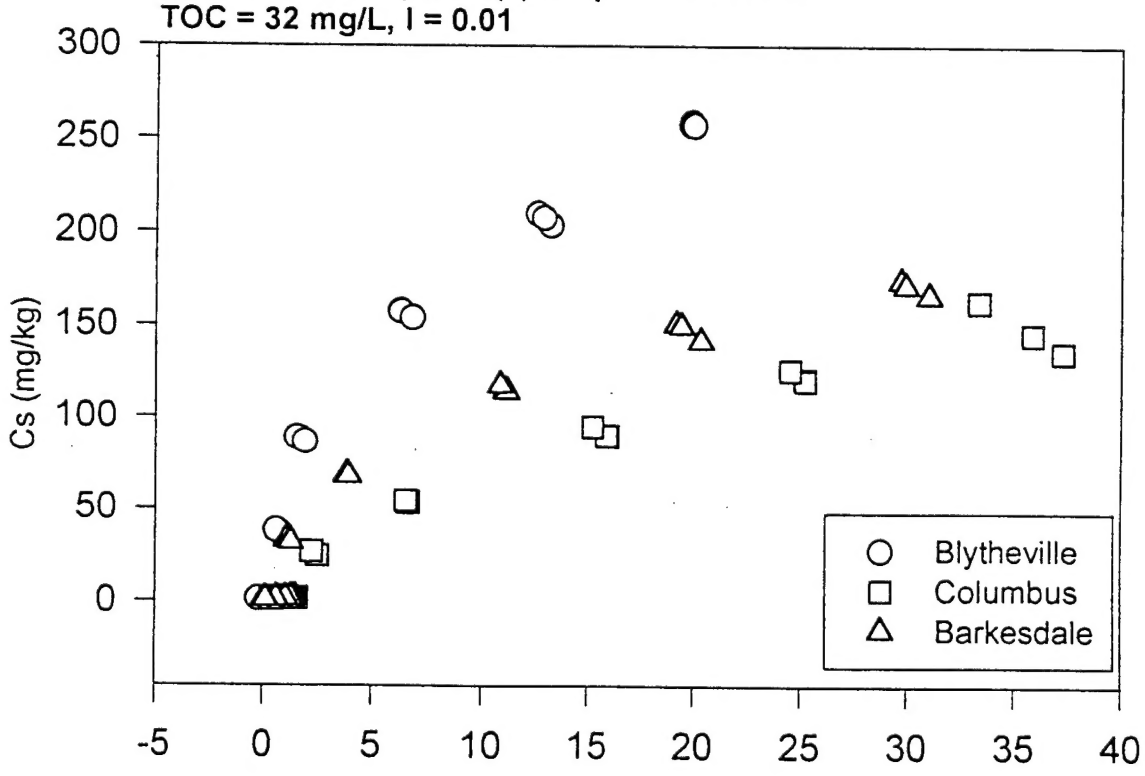

Figure 3. Freundlich Isotherm
Barkesdale, I = 0.01

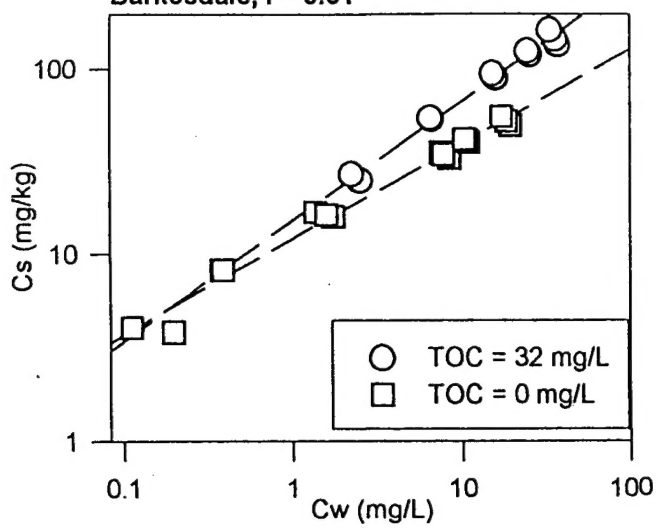

Figure 4. Freundlich Isotherm
Barkesdale, I = 0.1

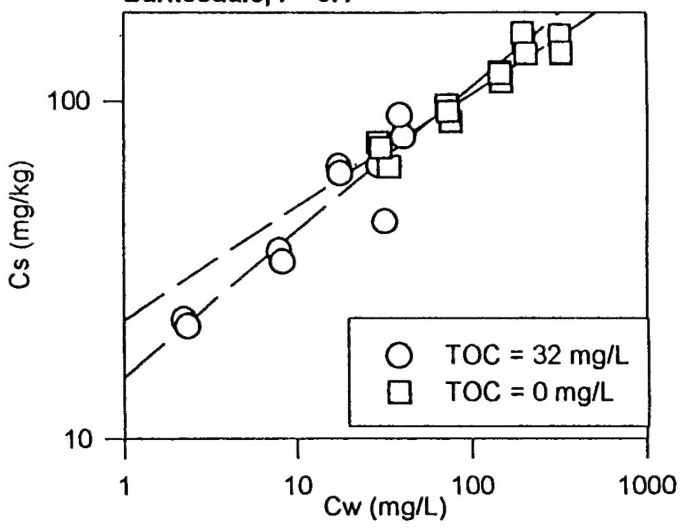

Figure 5. Freundlich Isotherm
Blytheville, I = 0.01

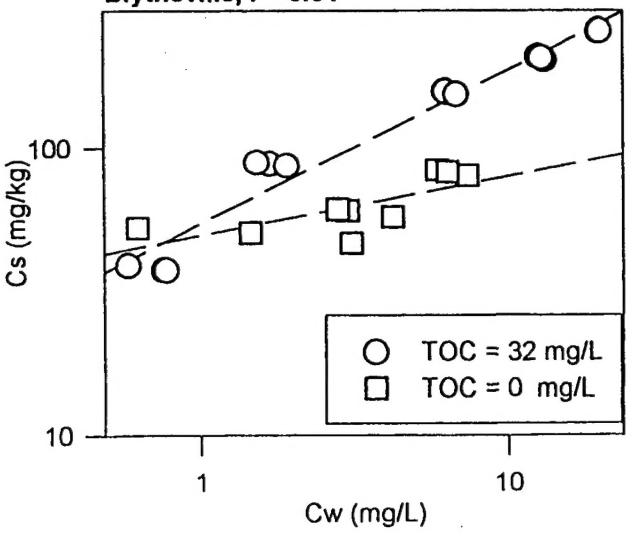

Figure 6. Freundlich Isotherm
Blytheville, I = 0.1

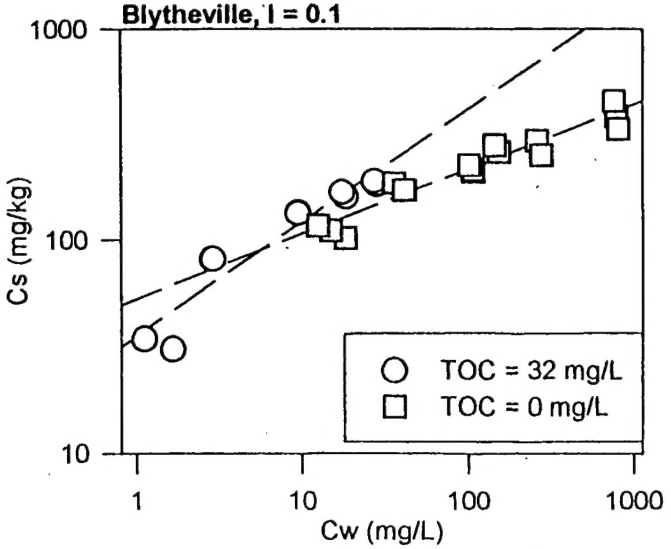

Figure 7. Freundlich Isotherm
Columbus, I = 0.01

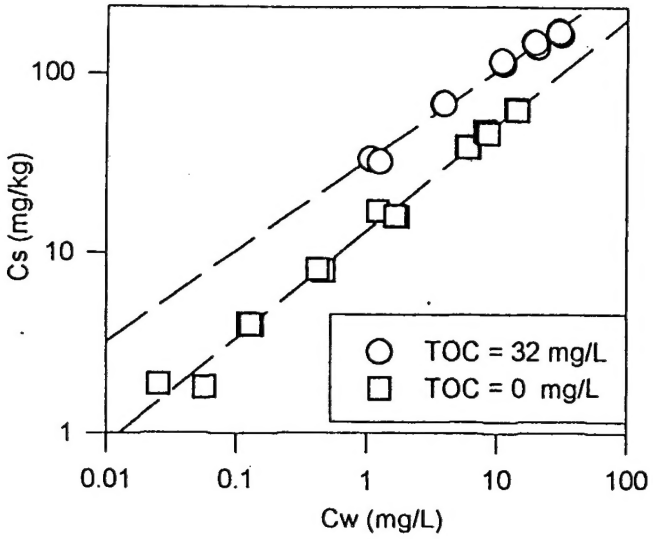

Figure 8. Freundlich Isotherm
Columbus, I = 0.1

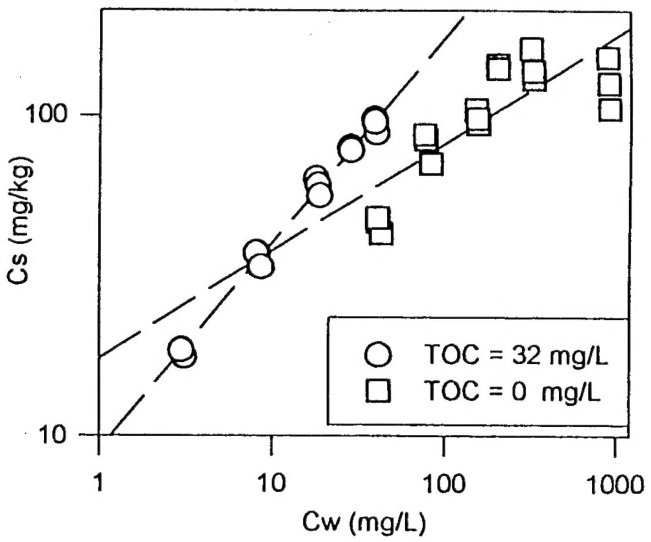

Figure 9. Sorption Isotherms: Barkesdale

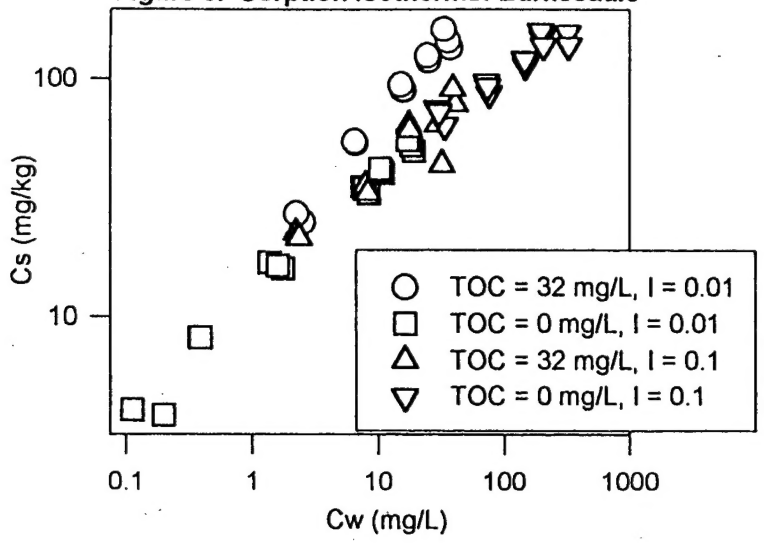

Figure 10. Sorption Isotherms: Blytheville

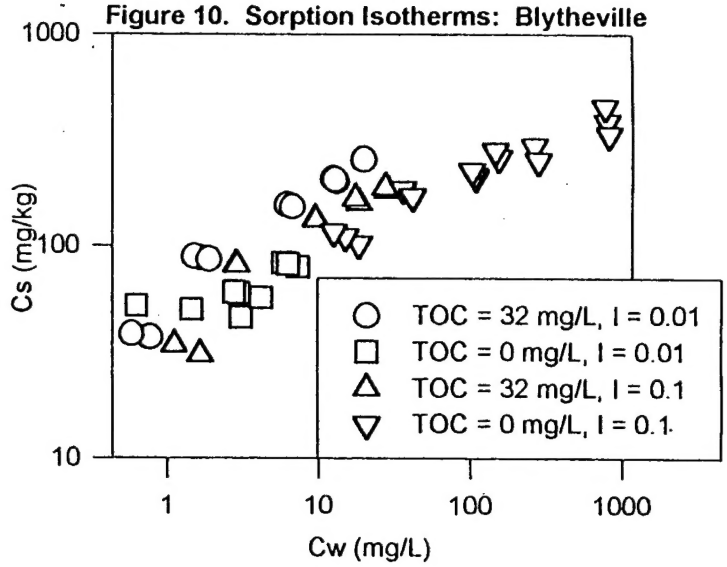
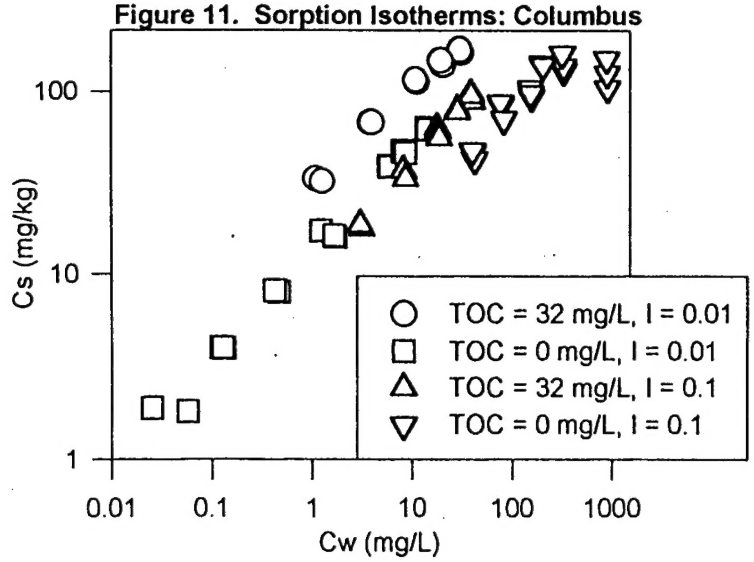
Figure 11. Sorption Isotherms: Columbus